UNITED STATES DEPARTMENT OF THE INTERIOR GEOLOGICAL SURVEY

Sulfur Isotopic Studies of the Stillwater Complex and Associated Rocks, Montana

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Open-File Report 89-76

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1988

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ABSTRACT

The Stillwater Complex, in south-central Montana, is a Late Archean layered, ultramafic to mafic intrusion emplaced into Middle to Late Archean metagraywacke, metashale, and ironformation. Sulfide minerals are concentrated near the base of the intrusion, in some chromitite layers, in podiform pegmatoids, in discontinuous discordant pods or pipes, and in numerous thin, stratiform layers. This investigation focusses on the isotopic composition of sulfur in metamorphosed sedimentary rocks, Stillwater-associated sills and dikes, sulfide accumulations near the base of the complex, and platinum-group element (PGE)-enriched sulfide mineralization that constitutes the J-M Reef and the Picket Pin deposit.

The δ^{34} S values for 233 samples analyzed in this study have a mean of 0.4 per mil, a standard deviation of 1.7, and maximum and minimum of -3.8 and 7.8 per mil. Despite the very narrow range of values, inspection of the data show, and analysis of variance calculations confirm that the analyses comprise three distinct groups. These groups are: 1) metagraywacke and metashale (mean 2.8 per mil); 2) iron-formation, Stillwater-associated sills and dikes, and basal sulfide accumulations in the complex (mean -0.7 per mil) and 3) disseminated sulfide minerals that occur above the basal accumulations in the Stillwater Complex (mean 1.2 per mil). The isotopic composition of sulfur of the basal sulfide accumulations indicates that assimilation of substantial amounts of sulfur from iron-formation could be an important mechanism for the formation of the basal sulfide deposits. This is consistent with the low tenor of the basal sulfide ores.

INTRODUCTION

Sulfur isotopic studies of magmatic sulfide deposits have demonstrated the importance of the assimilation of crustal sulfur in the formation of some magmatic sulfide deposits (Mainwaring and Naldrett, 1977; Ripley 1981; Godlevskii and Grenenko, 1963). Sulfide minerals are present in most of the Stillwater Complex cumulates (0.000x to 0.00x vol %) and are notably concentrated in some intervals (0.1 to 100 vol %). Despite this, very few sulfur isotopic analyses have been done on Stillwater Complex rocks. Early studies by Thode and others (1962) and Smitheringale and Jensen (1963) focussed on six samples from near the base of the complex; they reported an average δ^{34} S value of 1.6 per mil and a range from 0 to 5.9 per mil.

The purpose of this study is to characterize the isotopic composition of sulfur in rocks from the Stillwater Complex, Stillwater-associated sills and dikes, and metasedimentary rocks intruded by the complex. Samples from the complex represent four major mineralized intervals: 1) disseminated to massive Fe, Cu, Ni sulfide accumulations associated with the Basal series in the Mountain View, Nye Basin, and Iron Mountain areas (Page, 1979; Zientek, 1983); 2) Ultramafic series disseminated to massive Fe, Cu, Ni sulfide accumulations in the Iron Mountain area (the Camp deposit); 3) the platinum-group element (PGE)-enriched disseminated sulfide mineralization that constitutes the J-M Reef (Todd and others, 1982; Barnes and Naldrett, 1985); and 4) the PGE-enriched disseminated sulfide mineralization that constitutes the Picket Pin deposit (Boudreau and McCallum, 1986). Results of the isotopic analyses are used to evaluate the source and evolution of sulfur in these rocks.

GEOLOGIC SETTING

The Stillwater Complex, figure 1, intrudes Middle to Late Archean metasedimentary rocks originally consisting of graywacke, shale, diamictite, blue-quartzite, and iron-formation. The Stillwater Complex and metasedimentary country rocks occupy a fault-bounded block in the northern Beartooth Mountains in south-central Montana. The majority of the metasedimentary rocks exposed in this block are metagraywacke; iron-formation, blue quartzite, diamictite, and metashale only crop out within 1.6 km of the base of the Stillwater Complex in a trend that is roughly concordant to the contact (Page, 1977; Page and Zientek, 1985). Detrital zircons from these metasedimentary rocks are at least 3,200 m.y. old (Nunes and Tilton, 1971; Lambert and others, 1985). Prior to intrusion of the Stillwater Complex, the metasedimentary rocks experienced at least 2 folding events (Page, 1979).

The metasedimentary rocks were contact metamorphosed by the Stillwater Complex (Page, 1977; Vaniman and others, 1980; Labotka, 1985); nearest the contact, mineral assemblages are representative of pyroxene-hornfels facies metamorphism. The prograde metamorphic minerals are quartz, magnetite, gruenerite, inverted pigeonite, and fayalite in iron-formation; and quartz, cordierite, hypersthene, plagioclase, and biotite in metagraywacke (quartz-bearing hornfels). Minerals in metashale (cordierite-hypersthene hornfels) are similar to those in graywacke with the exception that quartz, plagioclase, and biotite are subordinate or absent. Farthest from the contact, metagraywacke has been metamorphosed to quartz-biotite schist and includes rare cordierite, anthopyllite, and/or garnet.

Sulfide assemblages in the metagraywackes, metashales, and iron-formation are similar, consisting of pyrrhotite, pentlandite, and chalcopyrite in the pyroxene-hornfels facies zone. In the lower grade rocks farthest from the contact with the Stillwater Complex, pyrite is also present. Intergranular textures are most common, although centimeter-to meter-scale, semi-massive lenses of sulfide minerals can be found. Fracture-controlled sulfide mineralization is rare and may represent very local mobilization of sulfide minerals. The sulfur content of iron-formation and associated sulfide-bearing hornfels ranges from 0.01 to 25.9 weight percent; the average of 41 analyses is 3.2 weight percent. This contrasts markedly with metagraywacke and metashale where sulfur content ranges from <.01 to 6.03 weight percent with an average of 0.76 for 22 analyses.

The Stillwater Complex is a layered ultramafic to mafic intrusion approximately 2,700 Ma old (Page, 1977; DePaolo and Wasserberg, 1979). Nearly 5.5 km of layered stratigraphy of the Stillwater Complex has been exposed as a result of northward tilting of the complex during deformation in the Laramide. This succession of layered cumulates has been divided into five series and approximately 17 zones (fig. 2; Zientek and others, 1985). The five series divisions in stratigraphic order are Basal, Ultramafic, Lower Banded, Middle Banded, and Upper Banded. Sulfide minerals, typically pyrrhotite, pentlandite, and chalcopyrite, occur throughout the stratigraphic succession in proportions, and with textures, that indicate that they formed as a result of crystallization of an immiscible sulfide liquid.

The Basal series consists dominantly of orthopyroxene cumulate although cumulus plagioclase, olivine, augite, and chromite can be present in the lower part of this unit (Page, 1979; Zientek and others, 1985). Disseminated, matrix, and massive sulfide accumulations are typical of the Basal series; generally the proportion of sulfide minerals increases toward the base of the complex (Page, 1979).

The Ultramafic series is made up of rocks which contain various proportions of cumulus olivine, bronzite, and chromite (Jackson, 1961; Raedeke and McCallum, 1984). The chromite seams that occur in the lower subdivision of the Ultramafic series (Peridotite zone) have sulfide minerals associated with them; typically, the modes of sulfide minerals are reported to be 0.01 vol % or less (Page, 1971; Mann and others, 1985). Disseminated sulfide minerals are common in cyclic units that characterize the Peridotite zone; however, significant occurrences of matrix and massive sulfide are not. Matrix and massive Fe,Cu, Ni sulfide occurrences in the lower part of the Ultramafic series in the Iron Mountain area (Camp deposit) and massive sulfide lenses associated with the G chromitite in the Mouat Cr mine (Page and others, 1976) are notable exceptions. Pegmatoid pods that contain disseminated to matrix sulfide minerals and graphite occur locally near the top of the Ultramafic series (Volborth and Housely, 1984).

The Lower, Middle, and Upper Banded series are distinguished by the presence of cumulus plagioclase. The presence (or absence) and proportion of cumulus bronzite, augite, olivine, and inverted pigeonite, as well as charges in crystallization order, are the basis for subdivision of the Banded series (McCallum and other, 1980; Segerstrom and Carlson, 1982; Todd and others, 1982). At least nine sulfide-enriched intervals have been found in the Lower, Middle, and Upper Banded series (McCallum and others, 1980; Todd and others, 1982); the most notable are the PGE-enriched sulfide mineral occurrences referred to as the J-M Reef (Todd and others, 1982; Barnes and Naldrett, 1985) and the Picket Pin deposit (Boudreau and McCallum, 1986).

A suite of Stillwater-associated sills and dikes intrude the metasedimentary rocks beneath the base of the complex and are the best analogues available for modeling the parent magmas for the Stillwater Complex (Zientek, 1983; Helz, 1985). At least 5 distinct compositional types have been

recognized: 1) gabbronoritic diabase (group 1 of Helz, 1985), 2) olivine gabbroic diabase (group 6 of Helz, 1985), 3) high-Ti noritic diabase (group 4 of Helz, 1985), 4) high-Mg gabbronorite (group 2 of Helz, 1985), and 5) mafic norite (group 3 of Helz, 1985). These sills and dikes have only been found in the metashale units near the base of the complex. Disseminated sulfide minerals occur in all the sills and dikes; however, the common association of matrix and massive accumulations of sulfide minerals are restricted to mafic norite sills and dikes (Zientek, 1983). As with the Stillwater Complex, the sulfide minerals are dominated by pyrrhotite, pentlandite, and chalcopyrite and formed as a result of the crystallization of an immiscible sulfide liquid.

Sampling all sulfide mineral occurrences from the Stillwater Complex was beyond the scope of this study; only major concentrations of sulfide minerals were investigated. In addition, major lithologies of metasedimentary rocks and Stillwater-associated sills and dikes were sampled. In all, 233 samples were analyzed (table 1 and fig. 3).

METHODS

Depending upon grain size, sulfide minerals were concentrated by drilling with a dental drill or were removed from crushed whole rock by acid-extraction (Kiba reagent; Sasaki and others, 1979). H₂S liberated by acid extraction was first converted to CdS, and finally Ag₂S. SO₂ for isotopic analysis was prepared by burning either sulfide concentrates or Ag₂S in vacuum with excess CuO. δ^{34} S values are reported as per mil deviation from Canon Diablo troilite, with an analytical uncertainty of \pm 0.1 per mil.

RESULTS

 δ^{34} S values for the entire group of 233 sample range between -3.8 and 7.8, average 0.4, and have a standard deviation of 1.7 (table 2). The rather narrow range of values with a mean very close to the presumed mantle isotopic composition of sulfur is not an unexpected result for rocks between 2,700 and 3,200 m.y. old (Skyring and Donnelly, 1982; Monster and others, 1979). However, inspection of the data and an analysis of variance show that three statistically distinct groups of samples can be recognized (fig. 4). Sulfides from the first group, metagraywacke and metashale, have a mean value of 2.8 per mil. The second group consists of magmatic sulfide minerals which are concentrated near the lower margin of the complex, magmatic sulfide minerals within the Stillwater-associated sills and dikes, and sulfide minerals within iron-formation . This group has a mean value of -0.7 per mil. The third group has a mean value of 1.2 per mil and includes magmatic sulfide minerals within the Stillwater Complex, such as the J-M reef, which are not associated with the basal contact.

Metasedimentary Rocks

Samples of metagraywacke and metashale have a mean $\delta^{34}S$ value of 2.8 per mil and a standard deviation of 1.0 per mil. Samples of metagraywacke were collected from the innermost part of the contact aureole in the Mountain View area, from a septum separating medium- and coarse-grained quartz monzonite intrusions in the vicinity of Flume Creek, and from the Divide Creek area, where contact metamorphic effects are negligible and the regional metamorphic fabric is preserved. Samples of the metashale (cordierite-hypersthene hornfels) come from the innermost part of the contact aureole in the Mountain View area. There is no statistical difference in $\delta^{34}S$ values between samples of metagraywacke and those of metashale. Values in metamorphic rocks are interpreted to reflect values of the protoliths; there is no change in $\delta^{34}S$ with metamorphic grade according to these data.

The isotopic composition of sulfur in iron-formation is approximately 4 per mil lower than sulfur in metashale and metagraywacke. Samples of iron-formation have a mean δ^{34} S of -0.8 per mil with a standard deviation of 0.8 per mil. These samples come from the Iron Mountain and Crescent Creek areas and show mineral assembleges typical of pyroxene hornfels metamorphism.

The small deviation of the mean $\delta^{34}\mathrm{S}$ from zero per mil is typical of sulfide minerals in Archean sedimentary rocks (Monster and others, 1979; Skyring and Donnelly, 1982). In younger rocks, $\delta^{34}\mathrm{S}$ values of sulfide minerals derived from bacteriogenic H₂S can provide a record of the presence of sulfate-reducing bacteria in sedimentary rocks, usually manifested by a spread of $\delta^{34}\mathrm{S}$ values that are enriched in $^{32}\mathrm{S}$. In rocks older than 2,350 Ma, the approximate time when the oxygenic weathering cycle was established (Cameron, 1982), the $\delta^{34}\mathrm{S}$ values of sedimentary rocks do not clearly indicate the presence of sulfate-reducing bacteria and commonly have $\delta^{34}\mathrm{S}$ values close to zero. This suggests that the ultimate source of sulfur for the Stillwater metasedimentary rocks was magmatic and mantle derived; the immediate source of sulfur may have been volcanic exhalations or detrital sulfide that survived weathering in an oxygen-poor atmosphere.

Stillwater Complex

Samples from the J-M Reef, the Picket Pin deposit, and the first cyclic unit of the Peridotite zone in the Mountain View area have a mean δ^{34} S value of 1.2 with a standard deviation of 1.4 per mil. These values are well within the range of -1 to 2 per mil and the average of 1.3 per mil reported by Ohmoto and Rye (1979) for mafic and ultramafic igneous rocks.

The J-M Reef, an interval containing sulfide minerals and other phases enriched in PGE is approximately in the middle of the Lower Banded series (fig. 2; Todd and others, 1982). The Reef occurs within the Olivine-bearing I zone, a complex unit containing troctolitic and anorthositic rocks, underlain by gabbronorites, norites, and anorthosites of the Gabbronorite I zone and overlain by norites of the Norite II zone. Samples from the reef have a mean δ^{34} S value of 1.0 per mil and a standard deviation of 1.2. Samples collected along the strike length of the J-M Reef show no systematic variability in the isotopic composition of sulfur.

The Picket Pin deposit consists of a number of sulfide-enriched layers, lenses, and disconformable pipes that occur in the upper part of the Anorthosite II zone and the lower part of the Olivine-bearing zone V (fig. 2). Boudreau and McCallum (1985) categorized the sulfide accumulations as PGE-poor or PGE-bearing. Typically, the PGE-poor sulfide accumulations occur in medium-grained anorthosite at the top of the Anorthosite II zone (mean δ^{34} S 1.0 per mil) and in Olivine-bearing zone V (mean δ^{34} S 1.6 per mil) and form numerous, thin, locally continuous layers. The PGE-bearing sulfide mineral accumulations (mean δ^{34} S 2.4 per mil) occur as discontinuous lenses or discordant pipes in coarse-grained anorthosite which underlies the medium-grained anorthosite that forms the top of the Anorthosite II zone. The PGE-bearing sulfide accumulations may owe their origin, in part, to the migration of volatile-enriched intercumulus melt (Boudreau and McCallum, 1985). The stratified PGE-poor sulfide accumulations may have resulted from differential rates of silicate and sulfide accumulation in gravity-stratified units (Foose, 1985). Despite the differences in occurrence, composition, and mode of formation, no statistically significant variations in δ^{34} S values were observed between the PGE-poor or PGE-bearing sulfide accumulations.

The samples from the first cyclic unit of the Peridotite zone of the Ultramafic series in the Mountain View area are sparsely mineralized and have a mean δ^{34} S of 2.3 per mil. They contain trace quantities of sulfide minerals that presumably result from the exsolution and crystallizations of small amounts of sulfide liquid from a magma saturated with sulfur. A complete cyclic unit in the Peridotite zone begins with a basal olivine cumulate, which may or may not contain a chromite seam, that grades upward into a bronzite-olivine cumulate, and finally into a bronzite cumulate (Jackson, 1961). The cyclic units are probably products of partial fractional crystallization from a batch of basaltic magma. As is typical of many of the cyclic units in the Peridotite zone, the first

cycle in the Mountain View area is incomplete, beginning with an olivine cumulate and grading upwards into a bronzite-olivine cumulate.

It is rather remarkable that sulfur isotope values of sulfide occurrences within the Stillwater Complex that are so widely separated in stratigraphic section and proposed to originate by very different processes (sulfide liquid exsolution as result of partial fractional crystallization of sulfur saturated magma; the mixing of magmas; and migration of a volatile-enriched intercumulus melt phase) are statistically indistinct. This may suggest that this part of the Stillwater Complex had access to a very uniform S reservoir.

Sulfide accumulations in the Basal series, Peridotite zone, and the Stillwater-associated sills and dikes

Sulfide accumulations at the base of the Stillwater Complex and in Stillwater-associated sills and dikes have a mean $\delta^{34}S$ value of -0.5 and a standard deviation of 1.2 per mil. These results are well within the range of values expected for mantle-derived sulfur in mafic and ultramafic rocks. However, these sulfide minerals are consistently enriched in ^{32}S relative to the disseminated sulfide minerals in the metagraywacke and metashale, and other sulfide occurrences in the Stillwater Complex, such as the J-M Reef and the Picket Pin deposit. Sulfide minerals in iron-formation are similarly enriched in ^{32}S with a range of -2.6 to 0.6 per mil and a mean value of -0.8.

Samples of the sulfide mineral accumulations in the Basal series have a mean $\delta^{34}S$ of -0.2 per mil and a standard deviation of 1.1. Disseminated, matrix, and massive sulfide mineralization in the Peridotite zone in the Iron Mountain area (Camp deposit) has mean $\delta^{34}S$ of -0.7 per mil and a standard deviation of 0.3.

The variety and extent of a suite of Stillwater-associated sills and dikes have only recently been documented (Zientek, 1983; Helz, 1985). Of the five distinct compositional types, the three most common were sampled in this study. Mafic norite sills and dikes in the Mountain View area, ranging from orthopyroxenite to gabbronorite, are enriched in disseminated to massive sulfide minerals. The sulfide minerals in the mafic norite sills and dikes are commonly concentrated towards the borders and in the adjacent metasedimentary rocks (Zientek, 1983). The isotopic composition of sulfur in these dikes and associated stringers in adjoining hornfels is the lightest observed in this study. There is no statistical difference in the isotopic composition of sulfur between sulfide minerals found in mafic norite intrusions and massive sulfide stringers in metasedimentary rocks that are associated with these intrusions (fig. 3). δ^{34} S values of disseminated sulfide minerals in two of the other sill and dike types, gabbronorite and olivine gabbro, range from -2.2 to 2.4 per mil. Mean δ^{34} S values for gabbronorite and olivine gabbro are -0.3 and 0.0, respectively.

DISCUSSION

In general, results of this study are consistent with what is alreadly known about the isotopic composition of sulfur in Archean metasedimentary rocks and mafic and ultramafic igneous rocks; δ^{34} S values are close to mantle values of 0 per mil and show low variance. One feature that deserves further consideration is the enrichment in 32 S in sulfide minerals in mafic norite sills and dikes and in earliest-formed sulfide minerals in the Stillwater Complex. The isotopic composition of sulfur in sulfide accumulations found near the base of the Stillwater Complex is indistinguishable from that of iron-formation or has values intermediate between those typical of iron-formation and disseminated, magmatic sulfide accumulations found higher in the Stillwater Complex (fig. 4). Three processes could produce the shift in isotopic composition of sulfide minerals found near the base of the complex and in the mafic norite sills and dikes: 1)

emplacement of magmas characterized by distinct sulfur isotopic values, 2) magmatic fractionation of the sulfur isotopes or 3) assimilation of ³⁴S-depleted sulfur from iron-formation.

Emplacement of a sulfide-enriched, isotopically lighter magma near the base of the Stillwater Complex could explain the unique composition of some of the basal sulfide accumulations. Numerous investigations have documented the importance of repeated injection of new magma in the petrogenesis of ultramafic to mafic layered intrusions, (Barnes and Naldrett, 1986; Campbell and others, 1983; Irvine and others, 1983; Lambert and Simmons, 1987 and 1988; Raedeke and McCallum, 1984; Sharpe, 1981 and 1985; Todd and others, 1982). These magmas may have been derived from different source regions in the mantle and lower crust so there is no reason to assume that each pulse of magma would have identical sulfur isotopic compositions. Changes in crystallization order and mineral fractionation trends suggest the rocks that constitute the Basal series may have had a parent magma different from cumulates that comprise the overlying Ultramafic series.

There are several studies that suggest that sulfur isotopes may factionate as a result of magmatic processes even though, based on equilibrium fractionation factors, no fractionation is predicted at magmatic conditions of approximately 900-1,000°C and fO2 too reduced for oxidized sulfur species (Ohmoto and Rye, 1979). Early studies suggested that early formed basal disseminated to massive sulfide accumulations are depleted in ³⁴S relative to magmas from which they segregated (Shima and others, 1963). Results from the Inziwa sill, South Africa showed a weighted mean δ^{34} S of 1.0 for the sill whereas the basal sulfide accumulations had δ^{34} S values that ranged from -2.5 to -3.0. For Archean layered sills in the Deer Lake Complex, Minnesota, sulfur isotopic differences of up to 2 per mil exist between earlier-formed chalcopyrite-rich pyroxenite units (isotopically heavy) and overlying chalcopyrite-poor gabbro units (isotopically light) (Ripley, 1983). For Sudbury ore deposits, sulfide minerals formed from residual Cu-rich liquids are isotopically heavier than Fe-rich sulfide minerals which crystallized earlier as part of a monosulfide solid solution (Naldrett, 1981). In our study, a chalcopyrite-segregation derived from a massive sulfide accumulation associated with a mafic norite sill or dike shows a similar isotopic shift (see sample 368-307A 595; table 1). δ^{34} S for the chalcopyrite segregation is -1.8 per mil compared to -3.3 per mil for the pyrrrhotite-rich massive sulfide associated with it. This suggests that sulfur isotopic variations resulting from the fractionation of silicate or sulfide liquids can produce isotopic shifts on the order of several per mil.

Finally, sulfur addition to the magmas by assimilation from local crustal sources may have resulted in formation of basal deposits with isotopic compositions at variance with the rest of the complex. This type of process has been well documented for sulfide deposits at the Duluth Complex (Mainwaring and Naldrett, 1977; Ripley 1981); Noril'sk Talnahk (Godlevskii and Grinenko, 1963; Grenenko, 1985); and the Bushveld Complex (Buchanan and others, 1981). In these examples, magmatic ores have sulfur isotope values that show significant deviation from 0 per mil and are shifted toward the composition of sulfur in nearby crustal rocks. These results indicate assimilation of crustal sulfur which ultimately led to the exsolution of immiscible sulfide liquids from the magma.

Unfortunately, in the case of the Stillwater Complex, the isotopic composition of sulfur alone is insufficient to select one of the models. However, bulk composition of the Fe, Cu, Ni ores supports the addition of sulfur to the Stillwater magma.

The tenor of the ores found near the base of the complex are quite low relative to other magmatic sulfide deposits; Cu and Ni concentrations calculated to 100 per cent sulfide for the sulfide accumulations in the Peridotite zone, Basal series, and mafic norite sills and dikes rarely exceed 2 and 4 wt %, respectively (fig. 5). These numbers are derived from results of selective sulfide leach studies reported in Page and Simon (1978) and other information summarized in table 3. The data plotted in figures 5 and 6 are a subset of a larger information set; however, only those determinations that had reasonable calculated total S in 100 per cent sulfide (greater than 30 wt %) and for which values of R (mass ratio of silicate liquid to sulfide liquid) independently calculated for Cu and Ni were in general agreement (IRCu-RNi| less than 200).

If we can approximate the composition of the magma from which the immiscible sulfide liquids exsolved, then an estimate for the initial Ni and Cu contents (X_i^0) of the silicate magma as well as the distribution coefficient of Ni and Cu between the silicate magma and the sulfide liquid (D_i) can be made. Given the final concentration of Ni and Cu in the immiscible sulfide liquid (Y_i) , R, a measure of how much silicate liquid an immiscible sulfide liquid has equilibrated with, can be calculated from the a modified version of the Nernst distribution equation:

$$R = \frac{(D_i^{a} - 1)}{(D_i - D_i^{a})}$$

where D_i^a is the apparent distribution coefficient and is equal to the final concentration of an element in the sulfide liquid (Y_i) divided by the initial concentration of that element in the silicate magma (X_i^o) (Campbell and Naldrett, 1979; Campbell and Barnes, 1984).

The parental magmas for the Basal series and the lower part of the Ultramafic series are best represented by group 2 high-Mg gabbronorites or group 3 mafic norites of the Stillwater-associated sills and dikes (Helz, 1985). Because group 3 mafic norites have high sulfide mineral contents, Ni and Cu estimates for the initial silicate liquid can not be obtained by direct analysis of the rocks; therefore estimates for the initial Ni and Cu contents of the magma (250 ppm for Ni and 120 ppm for Cu) are based on published information for group 2 high-Mg gabbronorites (Helz, 1985). Distribution coefficients appropriate for basaltic magmas ($D_{Cu} = 200$; $D_{Ni} = 250$) were used in the calculation of R for the basal sulfide accumulations (Rajamani and Naldrett, 1978; Naldrett, 1981). The results of these calculation are shown in figure 6, wherein calculated values of R rarely exceed 400 and generally are less than 200.

The results of similar calculations for magmatic sulfide deposits associated with representative Archean and Proterozoic komatiites, the J-M Reef, and the Talankh deposit are illustrated in figure 5. The curves show how the composition of an immiscible sulfide liquid varies as a function of the R value for differing bulk compositions of the initial silicate liquid. Symbols on the curves correspond to log R values of 1 (nearest the origin), 2, 2.5, 3 and 5 or greater. Model parameters are summarized in table 4. Ni and Cu contents for examples of deposits corresponding to each model type are also shown for comparison.

R values of $10^{2.5}$ to 10^5 would account for the compositions of many magmatic sulfide deposits associated with komatiites. Magmatic deposits associated with mafic magmas such as the J-M Reef or the Talnakh deposit require R values in excess of 10^5 ; this contrasts dramatically with the values of $10^{2.5}$ or less required to model the low Ni and Cu contents of the basal sulfide accumulations at Stillwater.

Low values of R combined with the high modal abundance of sulfide minerals in the basal sulfide accumulations is suggestive of addition of sulfur to Stillwater magmas. The most likely source of sulfur is iron-formation that predates the Stillwater Complex. In-situ addition of sulfur from iron-formation is supported in part by correlation of $\delta^{34}\mathrm{S}$ values in basal sulfide deposits with the presence of iron-formation in the basement. The composition of sulfide minerals in the Basal series in the Iron Mountain, Nye Basin, and Benbow areas, and the Peridotite zone in the Iron Mountain area, where iron-formation is present in the footwall, is isotopically lighter than sulfide minerals in the Basal series and Peridotite zone at Mountain View, where no iron-formation is present.

It is clear that in-situ assimilation of sulfur was not the only process involved in precipitation of the sulfide deposits found near the base of the Stilwater Complex. There are several lines of evidence that indicate that Stillwater magmas responsible for the formation of sulfide deposits near the base of the complex were sulfur saturated and some carried an immiscible sulfide liquid in suspension at the time of intrusion. First, inclusions of sulfide minerals in the cores of cumulus

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crystals in the Basal series and in early formed crystals in mafic norite sill and dike rocks are interpreted to represent droplets of the immiscible sulfide liquid which were trapped at the time early-forming crystals were growing from the magma. Second, the interstitial sulfide minerals in the Basal series are gravity stratified; in other words, their abundance increases towards the floor of the complex. This would not be expected if the sulfide minerals had formed from an immiscible sulfide liquid which exsolved when the rock was nearly completely crystallized. Third, magmatic sulfide minerals are commonly concentrated towards outer margins of mafic norite sills and dikes, perhaps as a result of flowage segregation. Many of these mineralized sills and dikes occur in the Mouat Ni-Cu prospect in the Mountain View area where there is no iron-formation in the footwall. At least some of the sulfide-rich margins of mafic norite sills and dikes preserve quench textures in the intergrown silicate minerals (Zientek, 1983). This evidence suggests the magma that crystallized to form mafic norite sills and dikes and Basal series assimilated sulfur, were transported, and emplaced with an immiscible sulfide liquid in suspension.

CONCLUSIONS

The isotopic evidence supports a model of sulfur addition to the magmas (by sulfur assimilation from local crustal sources) from which the magmatic sulfide deposits found at the base of the Stillwater Complex formed . Sulfur in iron-formation appears to be a likely comtaminant. The low R-values of the immiscible sulfide liquid and the low tenor of the Fe-Cu-Ni ores at the base of the Stillwater Complex is consistent with addition of sulfur to the Stillwater magma.

ACKNOWLEDGMENTS

Appreciation is expressed to the management of the Anaconda Minerals Company and the Manville Corporation for their cooperation in this study and their permission to publish the results. Norman J Page and Roger W. Cooper provided samples or directly assisted in drill core sampling. The manuscript has benefitted from reviews by N.J Page, T.G. Theodore, and R.A. Zierenberg.

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Figure Captions

- Figure 1.--Simplified geologic and location map of the Stillwater Complex and adjacent areas. Modified from Page (1977).
- Figure 2.--Simplified stratigraphic column for the Stillwater Complex showing the position of reported sulfide mineral occurrences, highlighting those analyzed in this study. Modified from McCallum and others (1980); Page and others (1985); Zientek and others (1985).
- Figure 3.--Histograms showing the distribution of $\delta^{34}S$ values in the Stillwater Complex, Stillwater associated sills and dikes, and metamorphosed sedimentary rocks.
- Figure 4.--Box plots illustrating δ^{34} S summary statistics for samples analyzed in this study; the top and bottom of the boxes are the 25th and and 75th percentiles respectively. Whiskers extending above and below the box indicate the values of the 10th and 90th percentiles. Values that fall outside the 10th and 90th percentiles are plotted as circles. Notches on the side of the box indicate the 95th confidence interval about the median value.
- Figure 5.--Cu and Ni contents in 100 per cent sulfide of various magmatic sulfide ores. Curves illustrate how the composition of sulfide liquids in equilibrium with various hypothetical silicate liquids change as a function of R, the mass ratio of silicate liquid to sulfide liquid. Compositions of these model liquids and values of distribution coefficients used in these calculations are given in table 4. Symbols along the curves represent logR values of 1, 2, 2.5, 3, and 5 or greater. Sources of information: Naldrett (1981); Barnes and Campbell (1984); Page and Simon (1978); and table 3.
- Figure 6.--Calculated values of R_{Cu} and R_{Ni} for disseminated, matrix, and massive sulfide from sulfide accumulations in the Basal series, the Peridotite zone of the Ultramafic series, and mafic norite sills and dikes. Information derived from Page and Simon (1978) and table 3.

EXPLANATION

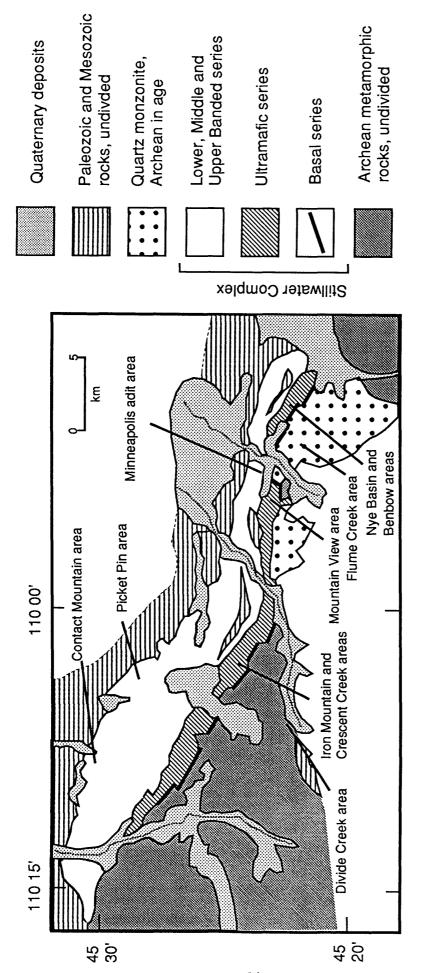
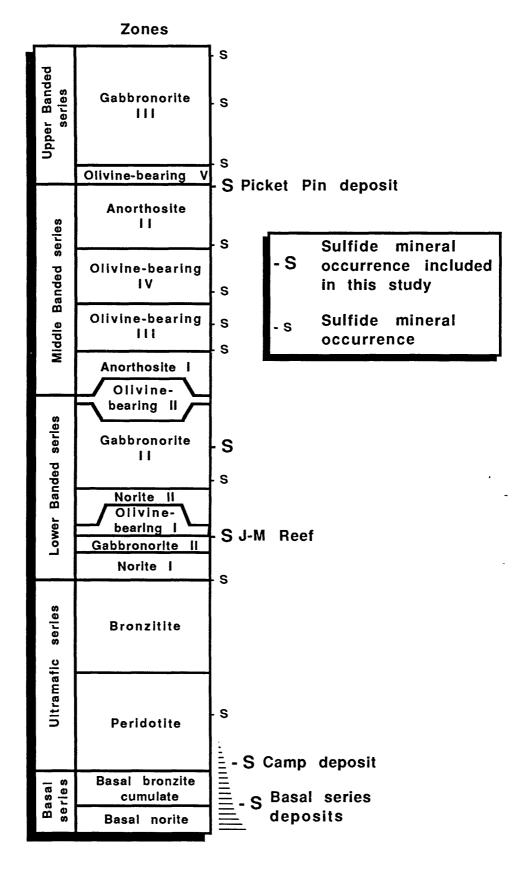
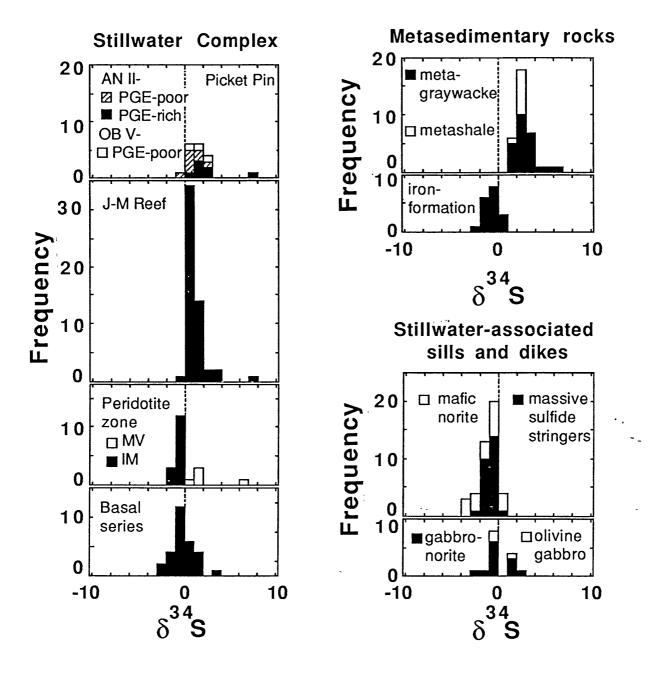
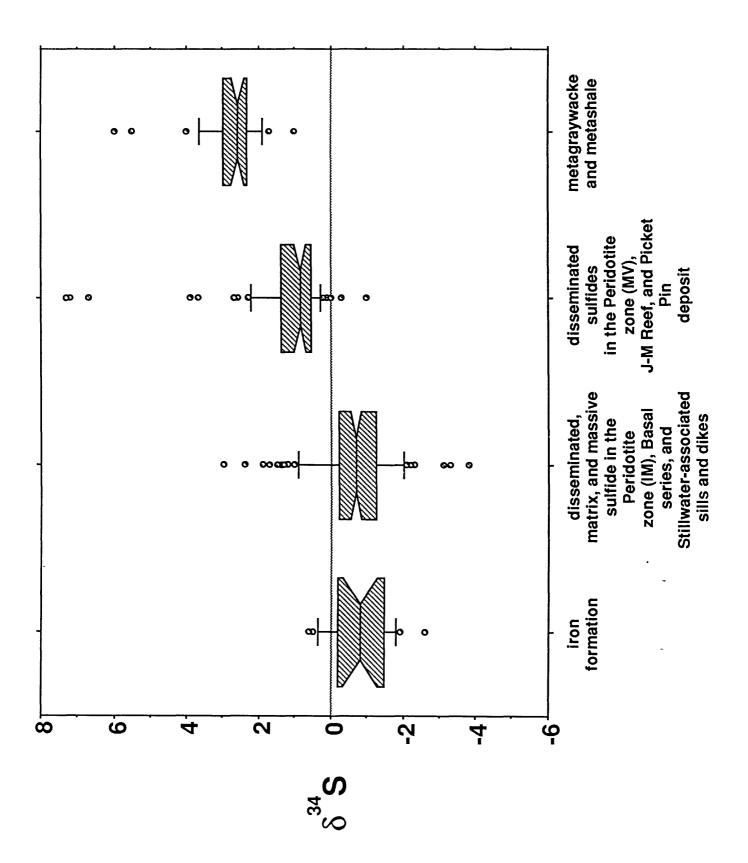
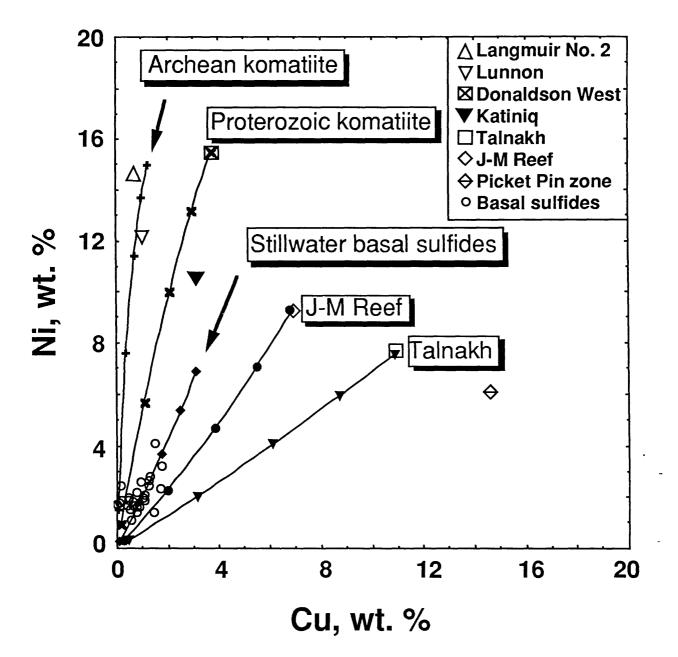


Figure 1









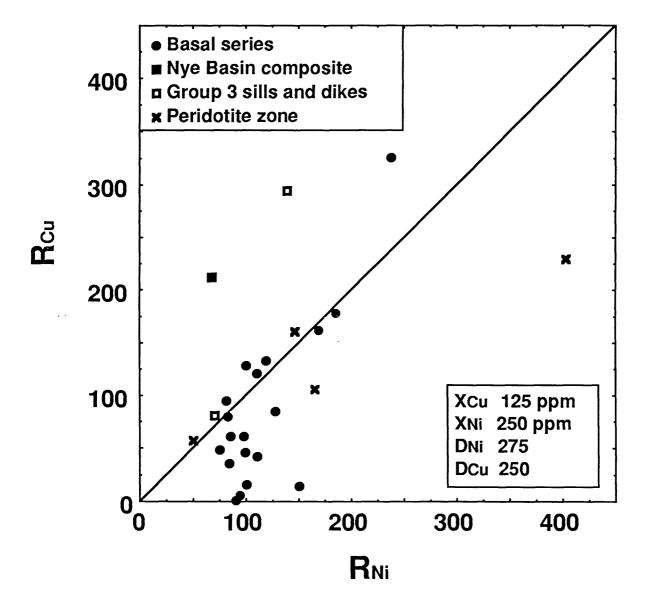


Table 1. δ^{34} s values of sulfides from rocks within and adjacent to the Stillwater Complex.

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M17	1048.	massive antifide approparion in coh	-2.0	7	402.	saive suifide	8-0-
NB-8	485.	מלווייני מנטונטטורים דיי	9.0-	٠.		າດກ	-0.7
ı		والمساوية والمسا		9			-0.8
		Stillwater Complex - Basal Series		9	534.8	00	-1.2
				355-61	540.2	00	-1.1
				9		OC 00000 0 0 00 00000 00000000000000000	
Iron Mountain area	tain are.	T. T.		9	551.	sample 8; massive sulfide; CP-rich	-0.2
355-59	585.8	l	4.0-	9-		Oc with matrix sulfide	-1:1
355-59	6.909		-0.7	9.	•	Oc with matrix sulfide	-0.5
355-59	625.	sulf1d	9.0-	355-64	719.5	foliated Oc with matrix sulfide	9.0
355-59	665.5	massive sulfide	7.1.	322-64	-1	UC With matrix sullide	0.01
77.77	7.700	77700		Mountain	View area		
Nye Basin		and Benbow areas		73-37	214.5	Rronaltead toine cumilate (ROC)	
NBI	181.5	bronzite-plasioclase cumulate (RPC)	-1.4	3.	303.	וייורכ - סיוי יווכ ימשמים יכ	1.7
NB1	204.5		4.0-	,	91.5	B0c	0.7
N 8 1	261.	bronzite cumulate (Bc)	-0.2	M17	232.	၁၀	6.7
NBI	325.	plagioclase-bronzite cumulate (PBc)	-1.3	M17	248.	00	1.3
- C C C	327.	metanorite np					
NB13	295.	Pc with matrix sulfide	-2.1				
887	860.	contact-8Pc/Bc	-2.1				

Sample no.		Sample type	834S	Sample no.		Sample Type	834S
S.	:111water 011	Stillwater Complex - Lower Banded series- Olivine bearing I zone		St 11	Stillwater Complex Olfvine-bea	er Complex - Lower Banded series- Olfvine-bearing I zone	
Minneapolis adit area	idit area			Janet claim block	block		
		- 1				- 1	
5102-E #2			1.2	77-74-14	152.0		0.0
7# 3-7016		Keer.		01-1/-//	203.0	Jan Reel	7.,
2104 × 1015		Keer;	· ·	01-4/-//	0./42		\
21.01.0			7•1	W07-C1-//	0.03		•
5110 ET		Reer Poof	4.0	M07-07-1/	0.4.0	The Park	• •
5112 EL		1-M Reef; Liotation conc.; non-magnetic	0 -	WZ-4/-//	185.0	J-A Keer	1.0
		Reef:	1.4	M7-7/-//	0.001		
Prod Dood				Brass Monkey claim block	r claim blo	ock	
	ור שו בש			77-74-6W	105.0	14 Reef	1.0
FPA-1		J-M Reef	0.5	77-74-6W	115.0	J-M Reef	0.8
FPA-2		J-M Reef	0.0	77-75-1WD	27.0	Jሗ Reef	0.3
				77-75-1WD	443.0	J-M Reef	0.0
)ck			77-15-7W	186.5	J-M Reet	0.8
2-61-11	762.5	J-M Reef	0.5	Olympia claim block	m block		
	960.5		0.5	nata natamira	400		
77-79-3	963.0		0.7	77-74-8W	113.5	J-M Reef	0.2
77-79-6	796.0			77-74-8W	121.0		0.8
77 70 6114	798.0	J-M Reef	0.7	77-75-2W	244.8	J-M Reef	0.8
77-79-16	332.0	LA Reel) r	77-75-2W	247.0	J-M Reef	0.0
85-80-3	487.0		1.0	Hamms claim block	block		
•							
Swan claim block	ock			77-75-24WB	54.0	J-M Reef	1.1
WT-79-77	44.5	J-M Reef	1.2	7/-/3-74MC	0.60	J-M keer	9.5
W-67-77	53.0		8.0	Dow claim block	ock		
11 10 011	7 6	The Keel		1			
W6-6/-//	87.0	TAN Reel	. c	77-79-1W	(88)40.5	J-M Reef	0.5
85-80-8	84.0		1.8	Blitz claim block	block		
	;						
Virginia ciaim block	n block			85-80-1	366.0	J-H Reef	0.4
77-79-1 2W	157.0	J-M Reef	2.6	Rlack Rutte area	901		
77-79-15W	91.0		9.0	2220	3		
77-79-15W	98.0	J-M Reef	0.7	76-4 IW	139.0	J-M Reef	7.0
77-79-17W	94.0	TAX Reef	-1.0				
Coors claim block	lock						
1000							
WE 2-51-11	23.0	J.A. Keer T.N. Roof	. 0				
77-79-20W	40.9		; -				
77-79-20W	47.9	Reef	0.3				
			1				

Table 1.

Table 1.

8 34S	
Sample no. Sample type	Stillwater Complex-Lower Banded series- Gabbronorite II zone

Mountain View area

Stillwater Complex - Middle Banded series-Anorthosite II zone - Picket Pin deposit Poorman - 5 Disseminated sulfides in Pc

Contact	Mounta	בו	ממפ	Contact Mountain and Ficket Fin areas	מוכס	
CM2	84	Pc	with	PGE-rich	sulfide	0.9
CM4	23	Pc	with	PGE-r1ch	sulfide	1.6
CM4	30.5	Pc	with		sulfide	2.1
CM4	31	Pc	with	PGE-rich	sulfide	1.1
CM7	125	Pc	with	PGE-rich	sulfide	2.3
PP1	638	Pc	with	PGE-rich		7.3
PP2	467	Pc	M th	PGE-r1ch	sulfide	1.1
CH1A	79.5	Pc	with	PGE-poor	sulfide	0.7
CH2	57	Pc	with	PGE-poor		0.9
PP 1	583	Pc	with	PGE-poor		2.1
PPl	621	Pc	with	PGE-poor		0.1
PP 1	628.5	Pc	with		sulfide	-0.3
PP2	430	Pc	with	PGE-poor	sulfide	1.1
PP2	435	Pc	Pc with		sulfide	1.2
PP?	197	ď	7	PCE-POOT		0.8

Stillwater Complex - Upper Banded series-Olivine-bearing zone V - Picket Pin deposit

Contact Mountain and Picket Pin areas

		With PGE-poor suifide 421 OPc with PGE-poor sulfide	421	PP2
1.7		with PGE-poor sulfide		
	(0 PC)	Olivine-plagioclase cumulate (416.5	PP2
2.7		14 Pc with PGE-poor sulfide	14	CM7

PGE, platinum-group elements; cp, chalcopyrite; po, pyrthotite.

deviation Standard 0.3 2.5 1.2 1.6 2.2 0.7 0.8 1.1 1.4 0.9 1.2 0.6 0.2 0.3 0.3 0.1 0.1 1.0 1.6 1.6 2.8 mean -0.3 0.0 -1.2 -1.4 maximum 0.0 6.0 0.3 0.3 0.0 3.0 3.0 3.0 0.3 0.3 0.3 0.3 7.2 7.3 7.3 7.3 minimum -2.1 -1.2 -1.2 -1.2 -1.2 -1.2 -0.3 -0.3 -2.6 1.0 1.0 -0.8 -2.2 -3.8 -2.2 ¤ 18 34 25 3 112 43 118 25 29 5 16 8 20 20 54 7 7 8 8 Summary Statistics of δ^{34} s values Stillwater-associated sills and dikes PGE-poor sulfides in AN II PGE-poor sulfides in OB V PGE-rich sulfide in AN II gabbronorite and norite Mafic norite and massive sulfides Metagraywacke and metashale Massive sulfide in cph Metamorphosed sedimentary rocks Metagraywacke (qph) Metashale (cph) olivine gabbro Mountain View Iron Mountain Mountain View Picket Pin deposit Iron Mountain Mafic norite Peridotite zone Nye Basin Iron-formation III Stillwater Complex Basal series Diabases J-M Reef Table 2. Unit II

1.1 0.5 1.1 0.9

Table 3.--Compositional information used to calculate Cu and Ni concentrations relative to 100 percent sulfide [Results of selective chemical dissolution of sulfides (method of Kock and others, 1986); Fe and S in weight percent; Co, Cu, and Ni in ppm. T.L. Fries analysist]

Sample	Stratigraphic unit	Rock type	Fe	පී	ਹੌ	ž	S
355-16-351	Peridotite zone	Olivine cumulate	26.0 960	096	3,950	11,000	14.9
355-61-501.5	Peridotite zone	Bronzite cumulate	4.43 194	194	1,150	3,150	2.81
355-64-682.1	Peridotite zone	Olivine cumulate	40.0	400	3,900	7,100	25.3
355-46-173	Basal series	Bronzite cumulate	1.69	54	375	800	1.07
355-64-760.2	Basal series	Bronzite cumulate	15.0	375	2,100	5,800	10.6
355-64-845	Basal series	Norite	8.90	237	1,920	4,100	6.07
384-333-247.8	Stillwater-associated sills and dikes	Mafic norite	9.3	178	1,200	2,220	90.9

[Results of whole rock analyses of composite samples. All elements reported as weight percent]

Sample number	Stratigraphic unit	Rock type	Fe	Fe Co Cu	Cn	ΪŽ	S
355-61-692.5 to 693.8	Peridotite zone	Massive sulfide	48.6 .10	.10	88.	1.67 27.0	27.0
USBM D 280 to to 314.5 ⁽¹⁾	Stillwater-associated Mafic norite sills and dikes	Mafic norite	47.7 .06	90.	.62	.85	.85 14.41
NB17A 724 to 802 ⁽²⁾	Lower part of Basal series and Stillwater- associated sills and dikes		28.2 .04	.04	.49	.47	.47 13.5

Data from Roby (1949)

²Data from Cooper (1980)

Table 4.--Initial Ni and Cu contents (X_i^o , in ppm) and distribution coefficients of Ni and Cu (D_i) between silicate magma and sulfide liquid used to model to variation of the composition of an immiscible sulfide liquid as a function of R

Model	$\mathbf{x_{Ni}}^{\mathrm{o}}$	$x_{Cu}^{\ o}$	Sul./Sil. D _{Ni}	Sul./Sil. DCu
Archean komatiite ⁽¹⁾	1,500	50	100	250
Proterozoic komatiite(1)	890	148	174	250
Talnakh ⁽¹⁾	276	436	275	250
Stillwater basal sulfides	250	125	275	250
J-M Reef	300	275	310(2)	250(2)

⁽¹⁾ Data from Naldrett (1981)

⁽²⁾ Data from Campbell and Barnes (1984)